



Europäisches Patentamt  
European Patent Office  
Office ur péen d s brev ts

⑪ Publication number:

**0 081 969**  
**A1**

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 82306529.7

⑮ Int. Cl.: **C 08 L 23/00, C 08 J 5/04**  
// (C08L23/00, 33/08, 95/00)

⑭ Date of filing: 08.12.82

⑯ Priority: 11.12.81 GB 8137530

⑰ Applicant: The British Petroleum Company p.l.c.,  
Britannic House Moor Lane, London EC2Y 9BU (GB)

⑲ Date of publication of application: 22.06.83  
Bulletin 83/25

⑳ Inventor: Aldred, Alan Charles George, The British  
Petroleum Company p.l.c. Chertsey Road,  
Sunbury-on-Thames Middlesex TW18 7LN (GB)

⑳ Designated Contracting States: BE DE FR GB IT NL SE

㉑ Representative: Harry, John et al, BP INTERNATIONAL  
LIMITED Patents and Licensing Division Chertsey Road,  
Sunbury-on-Thames Middlesex TW18 7LN (GB)

㉒ Blends of hardened extract with copolymers of olefin/alkyl acrylate.

㉓ This invention relates to a blend of an olefin/alkyl acrylate copolymer and hardened extract which has a saturated hydrocarbon content of not more than 10% by weight and articles made therefrom, eg linings for reservoirs and for water proofing roofs. The new products are easier to manufacture since they resist gelation, do not suffer from problems of shrinkage and are appreciably cheaper.

EP 0 081 969 A1

BLENDs OF HARDENED EXTRACT WITH  
COPOLYMERS OF OLEFIN/ALKYL ACRYLATE

The present invention relates to blends of hardened extract with copolymers of an olefin and an alkyl acrylate.

Elastomer blends containing hardened extract and chlorosulphonated polyethylene are known for use as waterproof membranes, eg for tank linings as shown by "Encyclopedia of Chemical Technology" 5 edited by Kirk-Othmer 2nd Edition, Volume 7, page 695.

Chlorosulphonated polyethylene elastomers have a number of disadvantages however. Thus for many purposes they have too low a modulus and tear strength.

10 It would be desirable to find a method of improving the physical properties of chlorosulphonated polyethylene elastomers and also a way of making a cheaper product based on modified polyethylene elastomers. When attempts are made to add bitumen to chlorosulphonated polyethylene to give a cheaper product, the resulting 15 material has an exceedingly low tensile strength and modulus.

Although useful compositions have been obtained by using, instead of bitumen, a product known as hardened extract or aromatic extract resin, such compositions cause gelation of the copolymer if high processing temperatures are used.

20 It has been found that these problems can be mitigated by replacing the chlorosulphonated polyethylene with an olefin/alkyl acrylate copolymer.

According to the present invention there is provided a blend of 25 an olefin/alkyl acrylate copolymer and hardened extract (as herein-after defined), said hardened extract having a saturated hydrocarbon

content of not more than 10% by weight.

According to yet another aspect of the present invention there is provided an article comprising an olefin/alkyl acrylate copolymer and hardened extract having a saturated hydrocarbon content of not more than 10% wt/wt.

The Olefin/Alkyl Acrylate Copolymer

The olefin/alkyl acrylate copolymers used in the present invention are suitably elastomers. Such copolymers and methods of production thereof are described, for instance, in US Patent

10 Nos 2953541 and 2953551. The olefin in the copolymer is preferably ethylene or propylene and the alkyl acrylate is preferably methyl acrylate, ethyl acrylate, propyl acrylate, pentyl acrylate, 2-ethyl hexyl acrylate or decyl acrylate. Copolymers of ethylene and ethyl acrylate are most preferred. In this case the ethylene polymer is 15 preferably a low density polyethylene. The olefin/alkyl acrylate copolymer in general, and the ethylene/ethyl acrylate copolymer in particular, suitably contains between 3 and 18% by weight, preferably between 8 and 18% by weight, of the alkyl acrylate.

The Hardened Extract

20 Throughout this specification 'hardened extract' means a material obtained by blowing a gas containing free oxygen into a petroleum extract at elevated temperatures, the petroleum extract having been obtained by the solvent extraction of a product of petroleum refining which is a distillate petroleum fraction or a de-asphaltered petroleum 25 residue, which product boils above 350°C at atmospheric pressure and which contains a major proportion of aromatic hydrocarbons.

The product of petroleum refining subjected to solvent extraction may be for example a vacuum distillate obtained by vacuum distillation of a residue from an atmospheric pressure distillation.

30 Alternatively, the product of petroleum refining may be obtained from vacuum residue (the residue of the vacuum distillation referred to above) after asphaltenes have been removed by precipitation with liquid propane. A product containing a major proportion of aromatic hydrocarbons may be derived by solvent extraction of mixtures of 35 distillates and residues.

A by-product of petroleum refining is vacuum distillate which is in the lubricating oil boiling range of 350°C to 600°C. Such vacuum distillates are well known to those skilled in the art.

5 The elevated temperature at which the gas containing free oxygen eg air is blown into the petroleum extract may for example be 200 to 350°C.

10 Examples of solvents which may be used to extract the petroleum distillate fraction are furfural, phenol and N-methyl pyrrolidone. The product subjected to extraction is substantially free from asphaltenes, and this extraction process must be distinguished from a process in which liquid propane is used to obtain from residues a product rich in asphaltenes. The latter process is sometimes described as a 'solvent' process.

15 Examples of such petroleum extracts are materials sold under the designation 'Enerflex' (Regd. Trade Mark) Process Oils by BP Oil International Limited, London. It is desirable that the hardened extract is prepared from a petroleum extract having a content of 'saturates' and 'aromatics' as determined by molecular-type analysis (clay-gel) ASTM D2007, of less than 15% by weight preferably less than 20 10% by weight for saturates, and suitably more than 75% by weight, preferably more than 80% by weight for aromatics.

25 The 'hardened extract' resulting from the air blowing referred to above is a solid material at room temperature. In order to obtain a hardened extract having the desired low content of saturated hydrocarbons it may be necessary to select a petroleum extract in which the saturated hydrocarbon content is low. The choice of a suitable petroleum extract can readily be made by the man skilled in the art on the basis of simple tests. The blowing with air may be carried out in the presence of a catalyst eg a metal halide 30 Friedel-Crafts catalyst such as ferric chloride, or without a catalyst.

35 The hardened extracts used in the present invention are to be distinguished from bitumens by the fact that they are made by either distillation or by de-asphalting a residue, followed by a solvent extraction, to produce a product which is substantially free of

0081969

asphaltenes, the asphaltenes only being introduced by blowing with a gas containing free oxygen. When crude oil is distilled to remove materials boiling up to the end of the gas oil range, the resulting residue, known as atmospheric residue, can be subjected to vacuum distillation to recover waxy distillates. The residue from this vacuum distillation is known as vacuum residue. The bitumen may be obtained directly from this residue or the residue may be air blown to produce a low penetration bitumen. Alternatively, the residue (either atmospheric or vacuum) may be treated with for example liquid propane to precipitate a bitumen layer. In all these cases the asphaltenes in the bitumen comes directly from the residue, and there is no intermediate material formed which is substantially free of asphaltenes.

The composition of hardened extracts and bitumens may be determined on the basis of their content of certain classes of material, namely 'asphaltenes', 'toluene insolubles', 'saturates', 'cyclics' and 'resins'. In this method asphaltenes are defined as that fraction which is precipitated by a large excess of n-heptane but which is soluble in toluene. Toluene insolubles are that fraction which is insoluble in toluene. Saturates are defined as that fraction which is eluted by n-heptane from an alumina/silica gel column, cyclics as that fraction which is eluted by toluene, and resins as that fraction which is eluted by a 50/50 toluene/absolute ethanol mixture.

Typical data on hardened extracts and bitumens are given in Table 1 where "HE" means 'hardened extract' and the number following "HE" is the softening point.

It will be seen that the hardened extracts have lower saturated hydrocarbon contents and much higher asphaltenes and toluene insolubles contents than either straight run or blown bitumens of equivalent softening point. The hardened extracts used suitably have asphaltenes plus toluene insolubles contents of at least 20% by weight. Preferably the content of asphaltenes alone is at least 20% by weight.

Hardened extracts having a range of softening points are readily

available. Thus hardened extracts having softening points ranging from 50°C to 200°C may be used. It is preferred to use hardened extracts having a softening point in the range 85-170°C. The softening point of hardened extract is measured by the ring and ball test used to determine the softening point of bitumens. This is described in Chapter 13 page 12 of "Petroleum Products Handbook" edited by Guthrie and published in 1960 by McGraw Hill.

5  
10  
15  
20  
25  
30  
35  
40

TABLE 1  
BROAD CHEMICAL COMPOSITION OF BLOWN BITUMEN AND HARDENED EXTRACTS

	115/15 Blown Kuwait Bitumen	85/25 Straight Run Bitumen	HE 140
<u>Softening Point</u> Ring and Ball °C	115	85	140
<u>Penetration at</u> 25°C mm/10	15.	25	less than 1
<u>BCC Analysis %</u>			
Saturates	18.1	10.0	9.6
Cyclics	33.2	55.3	28.0
Asphaltenes	32.5	7.1	50.4
Resins	14.9	26.1	12.2
Toluene Insolubles	2.1	1.5	40.5

Chlorinated Polyethylenes

The composition of the present invention may contain chlorinated polyethylenes in addition to the olefin/alkyl acrylate copolymer and the hardened extract.

Chlorinated polyethylenes with chlorine contents of from 20 to 48% by weight may be used. It is preferred to use chlorinated polyethylenes based on high density polyethylene having chlorine contents of from 25 to 40% by weight chlorine. Particularly preferred are chlorinated polyethylenes CPE 2552 and CPE 3614 which contain 25% and 36% by weight chlorine respectively and which are manufactured by Dow Chemical Company.

Other Optional Additional Ingredients

The compositions of the present invention may also contain particulate fillers that are commonly used in reinforcing rubber, eg calcium carbonate, carbon black, titanium dioxide, clay, talc, etc.

5 The use of these fillers can improve the tear strength of the blend. Fibrous fillers and coated fibrous fillers such as asbestos, cotton, polyester fibres, rayon fibres etc may also be used.

The compositions of the present invention may also contain various additives, eg to plasticise, to lubricate, to stabilise, to 10 enhance fire resistance and to prevent oxidation, providing these are compatible with the composition, ie do not readily separate from the composition after being mixed with it. Compatibility is particularly significant in the context of plasticisers. Examples of such plasticisers are aromatic extracts (this being the material from which 15 hardened extract is prepared), chlorinated paraffins, for example those having from 12 to 30 carbon atoms in the molecule, and esters, for example di-2-ethylhexyl phthalate or alkyl epoxy stearates. Plasticisers for use in olefin/alkyl acrylate copolymers are well known to those skilled in the art.

20 Compositions containing the above-mentioned optional additional ingredients may be used in either unvulcanised or vulcanised form.

Relative Quantities of Ingredients

The relative weights of olefin/alkyl acrylate copolymer and hardened extract used in the compositions of the present invention may 25 vary over a wide range but are preferably 4:1 to 1:10, more preferably 2:1 to 1:5, for example 1:1.

Where chlorinated polyethylene is present the weight of chlorinated polyethylene relative to olefin/alkyl acrylate copolymer is preferably in the range 1:9 to 4:1, more preferably 1:4 to 2:1, for 30 example 1:1.

The quantity of particulate filler, if present, is preferably in the range 1 to 250, more preferably 10 to 150 parts per hundred parts of the olefin/alkyl acrylate copolymer (and chlorinated polyethylene, if present), all parts being by weight.

35 The quantity of plasticiser, if present, is preferably in the

range 1 to 50, more preferably 5 to 25 parts by weight per hundred parts by weight of the olefin/alkyl acrylate copolymer (and chlorinated polyethylene if present).

5 The quantity of fibrous filler, if present, is preferably in the range 1 to 50, more preferably 2 to 25 parts by weight per hundred parts by weight of the olefin/alkyl acrylate copolymer (and chlorinated polyethylene if present).

#### Preparation of the Compositions

10 The compositions of the present invention may be prepared by any convenient method. Thus any of the methods used in compounding rubbers may be used, eg the methods using a Banbury mixer, or a 2-roll mill.

#### Uses of Compositions According to the Present Invention

15 Compositions according to the present invention are particularly useful when formed into articles, especially into sheets for lining reservoirs or for waterproofing roofs. Such sheets may be, for example, formed by moulding or by calendering between heated rollers. The compositions of the present invention may be also used to produce bituminous mastic backed products, polyester felt backed products and 20 laminates in which non-woven scrims may be used as reinforcements. Bitumen is compatible with the compositions of the present invention and causes no bleeding.

25 The invention will now be illustrated by the following Examples in which all parts are parts by weight.

25 The meaning of the various trade names and abbreviations used in these Examples is as follows:

	<u>Terms</u>	<u>Meaning</u>
30	Hypalon 45	A chlorosulphonated polyethylene containing 25% Cl and 1.0% of S produced by E.I. du Pont de Nemours.
35	He 140	A Hardened Extract having a softening point of 140°C.
	EEA 6178	An ethylene ethyl acrylate copolymer containing 10% ethyl acrylate and produced by BP Chemicals Limited.

	FFF Black	A fast extrusion furnace carbon black produced by Cabot.
	CPE 3614 'A'	A chlorinated polyethylene containing 36% chlorine produced by Dow.
5	Mistron talc	Pure magnesium silicate.
	Rigidex HDPE	High Density Polyethylene produced by BP Chemicals Limited.
	180/52	
	Edenol B35	An alkyl epoxy stearate plasticiser produced by Heikel et Cie.
10	Amine	Octadecylamine processing aid.

Examples 1 - 6

15 A composition was prepared by mixing all the ingredients (shown for the respective Examples in Table 2 below) in a 1-litre laboratory Banbury rubber mixer at 130-140°C for 10 minutes. The resulting mixture was then milled on a 6" x 12" two roll laboratory mill at 130°C for 60 minutes to assess the effect of extensive processing. No gelation occurred during the milling as evidenced by the smooth appearance of the sheet on the mill.

20 1 mm thick sheets from which samples for testing physical properties were cut, were prepared by moulding the composition taken from the mill for 5 minutes at 130°C and then cooling the sheets in the mould.

The ingredients used and the results obtained are shown in Tables 2 and 3.

25 Comparative Test (not according to the invention)

30 A composition was prepared by mixing all the ingredients shown in Table 2 in a 1-litre laboratory Banbury rubber mixer at 130-140°C for 10 minutes. The resulting mixture was then milled on a 6" x 12" two-roll laboratory mill at 130°C for 60 minutes. The mixture became rough in texture and very sticky on the mill. The mixture had gelled. 1 mm thick sheets from which samples for testing physical properties were cut, were prepared by moulding the composition taken from the mill for 5 minutes at 130°C and then coding the sheets in the mould.

35 The ingredients used and the results obtained are shown in Tables 2 and 3.

0081969

9

TABLE 2  
Ingredients (parts by weight)

(Total charge fed to the Banbury mixer was 1.1 kg in each cases, the proportions by weight being as before)

Example	EEA	CPE 3614A	HYPALON 45	HDPE 180/52	HE 140	BLACK FEP	TALC MISTRON	EDENOL B35	AMINE
1	40	60	0	0	85	40	0	8	1
2	50	50	0	0	85	40	0	8	1
3	60	40	0	0	85	40	0	8	1
4	40	50	0	10	85	40	10	8	1
5	50	50	0	0	90	40	0	8	1
6	50	50	0	0	85	40	10	8	1
Comparative Test	0	50	50	0	85	40	0	8	1

TABLE 3  
Physical Properties

Test Method	Dimensional stability	Brittle Temp.	Tensile strength	Elongation at break	Modulus at 300%	Test Strength	Shore 'A'
	DIN 53377	DIN 53361	BS 903 Part A2	BS 903 Part A2	BS 903 Part A2	BS 903 Part A3	BS 903 Part A26
Example No 1	1.5%	-20°C	7.4	670	4.2	38	69
2	1.0%	-25°C	6.3	720	3.8	41	72
3	0.5%	-22.5°C	6.4	620	4.5	41	74
4	0	-	6.0	600	4.7	40	78
5	0.5%	-22.5°C	6.3	710	3.7	39	72
6	0.5%	-20°C	5.8	670	4.0	42	71
Comparative Tests	14%	-25°C	8.3	580	5.6	40	62

From the above results, in particular by a comparison of the data in Example 2 with the Comparative Test, it can be seen that compositions containing ethylene/ethyl acrylate copolymer instead of a chlorosulphonated polymer were vastly superior showing no gelling and 5 possessing the desired characteristics such as high tensile strength, high elongation at break, low modulus and high Shore 'A' tests. Under the conditions used, the product from the Comparative Tests, in fact, gelled and vulcanised.

10

15

20

25

30

35

**Claims:**

1. A blend of an olefin/alkyl acrylate copolymer and hardened extract (as hereinbefore defined), said hardened extract having a saturated hydrocarbon content of not more than 10% by weight.
2. A blend according to claim 1 wherein the olefin in the copolymer  
5 is ethylene or propylene and the alkyl acrylate is selected from methyl acrylate, ethyl acrylate, propyl acrylate, pentyl acrylate, 2-ethyl hexyl acrylate and decyl acrylate.
3. A blend according to claim 1 or 2 wherein the copolymer is derived from ethylene and ethyl acrylate.
- 10 4. A blend according to claim 3 wherein the ethylene polymer is a low density polyethylene.
5. A blend according to any one of the preceding claims wherein the olefin/alkyl acrylate copolymer contains between 3 and 18% by weight of the alkyl acrylate.
- 15 6. A blend according to any one of the preceding claims wherein the relative weights of olefin/alkyl acrylate copolymer and hardened extract in the blend is in the range 4:1 to 1:10.
7. A blend according to any one of the preceding claims wherein the blend contains in addition a chlorinated polyethylene.
- 20 8. A blend according to claim 7 wherein the weight of chlorinated polyethylene relative to olefin/alkyl acrylate copolymer is in the range 1:9 to 4:1.
9. An article comprising an olefin/alkyl acrylate copolymer and hardened extract having a saturated hydrocarbon content of not more  
25 than 10% wt/wt.
10. An article according to claim 9 wherein said article is a bituminous, mastic-backed product incorporating non-woven scrims as reinforcements.

11. An article according to claim 9 wherein said article is a polyester felt backed product.

12. An article according to claim 9 wherein said article is a product incorporating non-woven scrims as reinforcements.

5

10

15

20

25

30

35



EUROPEAN SEARCH REPORT

0081969

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82306529.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
A	US - A - 4 210 567 (B. KÖSTERS) * Claims 1,2,11,14 * --	1,2	C 08 L 23/00 C 08 J 5/04// (C 08 L 23/00 C 08 L 33/08 C 08 L 95/00)
A	GB - A - 1 468 603 (E.I. DU PONT DE NEMOURS AND COMPANY) * Claim 1 * --	1	
A	KIRK-OTHMER "Encyclopedia of chemical technology" 3rd edition, vol 8, 1979 JOHN WILEY & SONS, New York, Chichester, Brisbane, Toronto pages 484-491 * Page 490 * ----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			C 08 L 23/00 C 08 L 33/00 C 08 J
The present search report has been drawn up for all claims			
Place of search VIENNA	Date of completion of the search 23-03-1983	Examiner TENGLER	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			